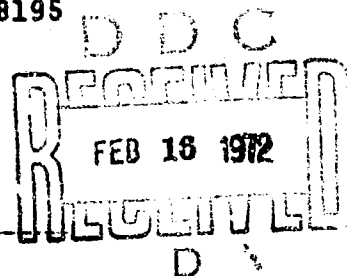Contribution from the Department of Chemistry
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KINETICS OF HYDROLYSIS OF OXYGEN DIFLUORIDE

By Sudhindra N. Misra and George H. Cady[*]

Abstract

Oxygen difluoride dissolves in water and reacts only very slowly with the solvent. In alkaline medium, however, the rate of hydrolysis is increased and follows the equation

$$\frac{d[OF_2]}{dt} = -k[OF_2]\{[OH^-]^{\frac{1}{3}}-0.0105\}$$

At 20° the constant, k, has the value 4.1×10^{-3}, when time is in seconds and concentrations are in moles per liter. The energy of activation is about 8.5 kcal per mol.

INTRODUCTION

The basic hydrolysis of oxygen difluoride has previously been studied, but under such conditions that the rate controlling step was the rate of dissolving of the gas rather than the rate of hydrolysis when in solution.[1]

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1. F. Ishikawa, T. Muroska and H. Hagisawa, Bull. Inst. Phys. Chem. Research, Tokyo, 12, 742 (1933).


In the present study, the rate of disappearance of dissolved OF_2 was measured. Substantially no gaseous phase was present in the system. The total reaction was $OF_2 + 2OH^- = O_2 + 2F^- + H_2O$. (1) Oxygen difluoride does not behave as the anhydride of an acid. It has only a low solubility in water[2] or even in cold 40% KOH.[3]

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2. O. Ruff and W. Menzel, Z. anorg. allgem. Chem., 198, 39 (1931).
3. R. A. Rhein and G. H. Cady, Inorg. Chem., 3, 1644 (1964).

None of its reactions are known to produce the recently discovered molecule, HOF.[4]

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4. M. H. Staudier and E. H. Appelman, J. Am. Chem. Soc., 93, 2349 (1971)
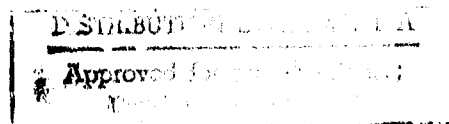
EXPERIMENTAL

Oxygen difluoride used in this study was a commercial product obtained from the Allied Chemical Company. When a sample of the gas was taken directly from the cylinder, its infrared spectrum showed no evidence for impurities. Fractional codistillation of a sample also gave indication of the presence of only one substance. In spite of this evidence for purity, the gas, before use in studies of its hydrolysis, was bubbled through 0.1M-NaOH to re- move SiF_4 and other acidic gases which might have been present. The base would have caused the introduction of some oxygen into the OF_2. This oxygen impurity should not have been harmful. Be- fore making a run, a solution of OF_2 was prepared by shaking a sample of the gas with water held in a two liter flask.

Apparatus - The reactor was a vessel of polypropylene having a volume of 1245 ml. The vessel was 18 cm. in diameter and had a tight, but removable lid equipped with polypropylene fittings to hold the following items: (1) a fluoride ion sensitive electrode made by Orion Research, Inc., model 94-09, (2) a reference electrode for use with the fluoride electrode, (3) and (4) a glass electrode and reference electrode for use in measuring pH, (5) a thermometer. A Teflon covered magnetic stir-bar was placed in the vessel and was rotated during a run by a magnetic stirrer placed under the ther- mostat bath. Measurement of pH was made with a Leeds and Northrup 7400 A2 series meter. The emf of the cell involving the F^- sensitive electrode was measured with an Orion Research Specific Ion Meter, Model 401.

Procedure - A measured amount of solution of OF_2 was transferred to the reactor. Other reagents as desired were also added, and

the reactor, before use in a run, was caused to be completely

filled with solution and closed with a loosely fitting plug.

The vessel was placed in water held at constant temperature to

within $0.1°$. After the solution reached constant temperature,

readings were made from time to time of the pH and F^- concentra-

tion. Many runs were made in buffered solutions containing sodium

carbonate, sodium bicarbonate, and enough sodium nitrate to give

a total ionic strength of 0.25 molar. In other runs the solution

was made alkaline with sodium hydroxide, and the pH was allowed

to change as the reaction occurred. A comparison of rate constants

obtained by the two methods indicates that the presence of ions

other than OH^- in the buffered solutions had little or no influence

upon the rate of hydrolysis of OF_2. Some of the runs were made

with solutions more alkaline than pH 11. Since the fluoride sen-

sitive electrode could not be used in this range, the concentra-

tion of dissolved OF_2 was measured by withdrawing a 25 ml sample

of solution and adding it to a solution of potassium iodide. After

adding dilute sulfuric acid in excess, the iodine was titrated with

sodium thiosulfate solution. To keep the reactor filled so that

OF_2 would not escape from solution, glass beads were added immedi-

ately after removal of the sample of solution. In runs involving

use of the fluoride ion sensitive electrode the concentration of

OF_2 was not observed directly. Along the course of a run, the

concentration of F^- ion was measured at intervals. At the termina-

tion of a run the solution was allowed to stand until substantially

all of the OF_2 had reacted. The molar concentration of dissolved

OF_2 at any stage of the run could then be calculated by consider-

ing it to be half as great as the increase in molarity of F^- from

that time until all of the gas had reacted.

During the course of the work the pH meter was tested frequently with buffer solutions. The fluoride sensitive electrode was also checked frequently using solutions containing F^- of known molarity, pH and ionic strength. Because of this method of calibration, the electrode as used gave F^- concentrations in moles per liter. From readings of the pH meter, the corresponding activities of OH^- in moles per liter were calculated. The fluoride-ion sensitive electrode behaved in the manner reported by the manufacturer toward F^- concentration and influence of ionic strength. Because of interference by OH^- ion, the electrode was not used at pH in excess of 11.

RESULTS

Observed data are represented within the limits of experimental accuracy in Figs. 1 to 4. Fig. 1 represents four runs at 20.0° using solutions buffered at different values of pH. These runs together with others not shown indicate that at constant pH and temperature the rate is directly proportional to the concentration of OF_2. Fig. 2 represents a run at 20.0° in which OF_2 reacted with a solution of sodium hydroxide while the pH was allowed to change as hydrolysis occurred. From the shape of the curve it is apparent that a decrease in the concentration of OH^- ion causes a decrease in the rate of reaction. If one draws a tangent to the curve at a selected value of pH, the slope is the same (within experimental accuracy) as a straight line in Fig. 1 for the same pH. Numerous runs of this type were made, some at pH values greater than 11.

At constant pH, the rate follows the equation $\dfrac{d[OF_2]}{dt} = -k'[OF_2]$

To evaluate k' as a function of [OH⁻], graphs were drawn in which k' was plotted vs. various powers of the molarity of OH⁻. Fig. 3 shows that at 20° in the pH range 9.6 to 11.5 the value of k' is directly proportional to $\{[OH^-]^{\frac{1}{3}}-0.0105\}$. The rate equation may, therefore, be written as

$$\frac{d[OF_2]}{dt} = -k[OF_2] \{[OH^-]^{\frac{1}{3}}-0.0105\}$$

In the evaluation of k' and k, time was measured in seconds. The straight line in Fig. 3 corresponds to k having a numerical value at 20°C of 4.1×10^{-3} when time is in seconds and concentrations are in moles per liter.

The three highest points in Fig. 3 were obtained using iodometric titration of dissolved OF_2 as it was reacting with a solution of NaOH. The other points were obtained using the fluoride-ion sensitive electrode as the dissolved OF_2 reacted either with a solution of NaOH or with a buffered solution containing Na_2CO_3, $NaHCO_3$ and $NaNO_3$. Most of these points were obtained for buffered solutions.

Runs were made using buffered solutions at pH = 10.0 at 25.0° and 30.0°. From these runs, values of k were calculated. Fig. 4 shows the relationship between lnk and the reciprocal of absolute temperature. The slope of the line in this figure corresponds to an energy of activation of 8.5 kcal per mole.
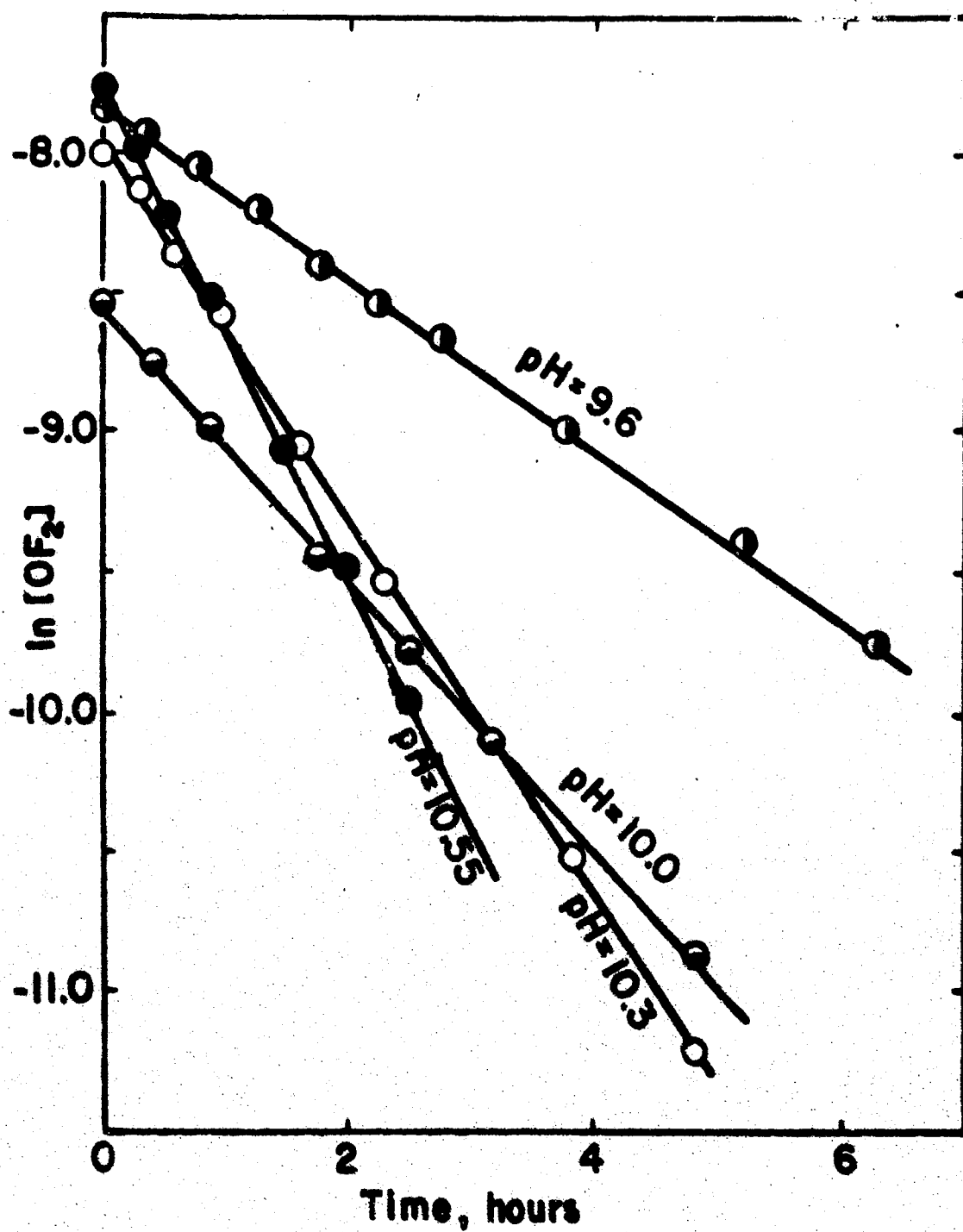
Fig. 1 — Rate of hydrolysis at 20.0° in buffered solutions.
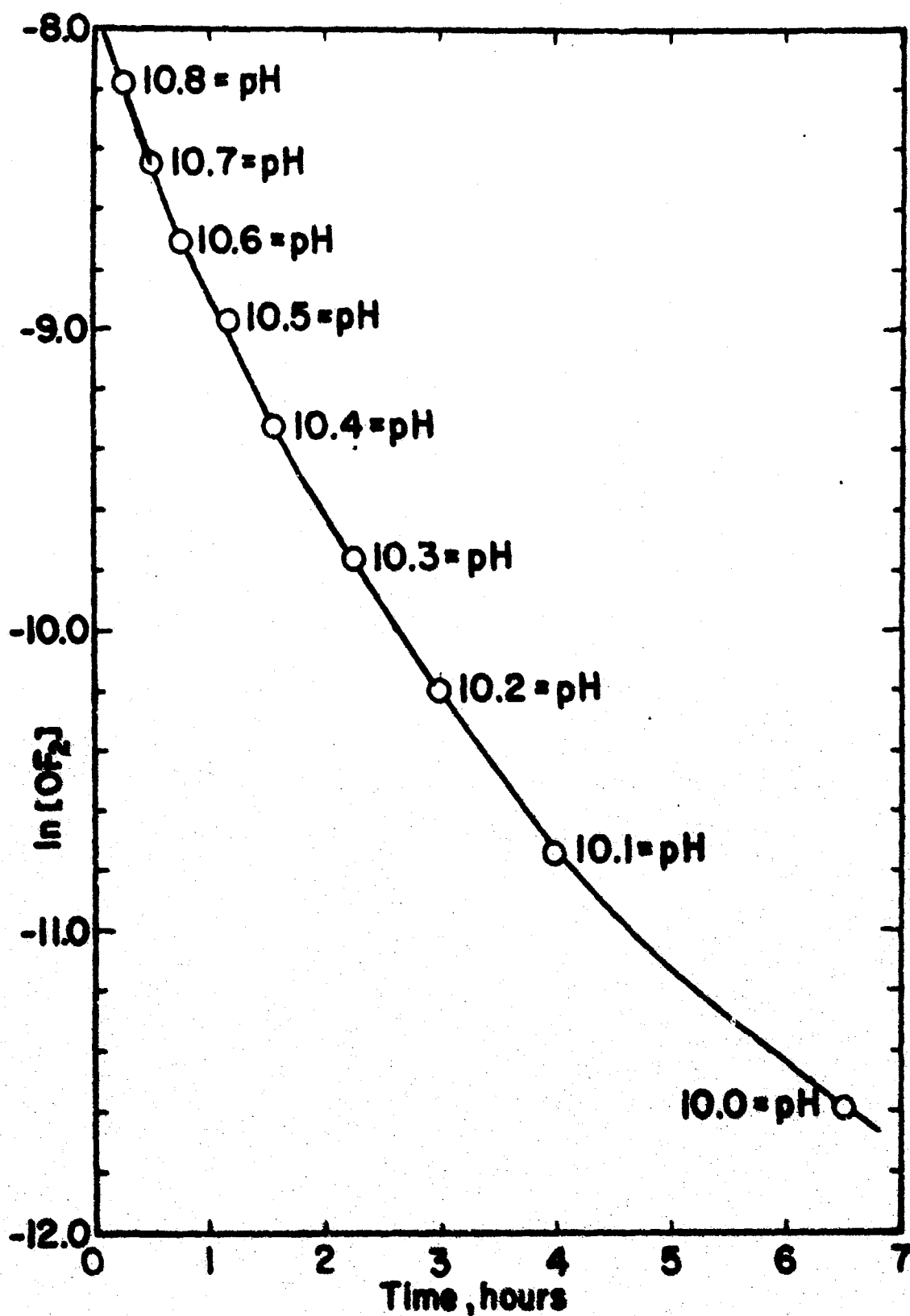
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Fig. 2 - Rate of hydrolysis of OF_2 in a solution of sodium hydroxide at 20.0°. Concentrations of OF_2 and of OH^- decrease as time passes
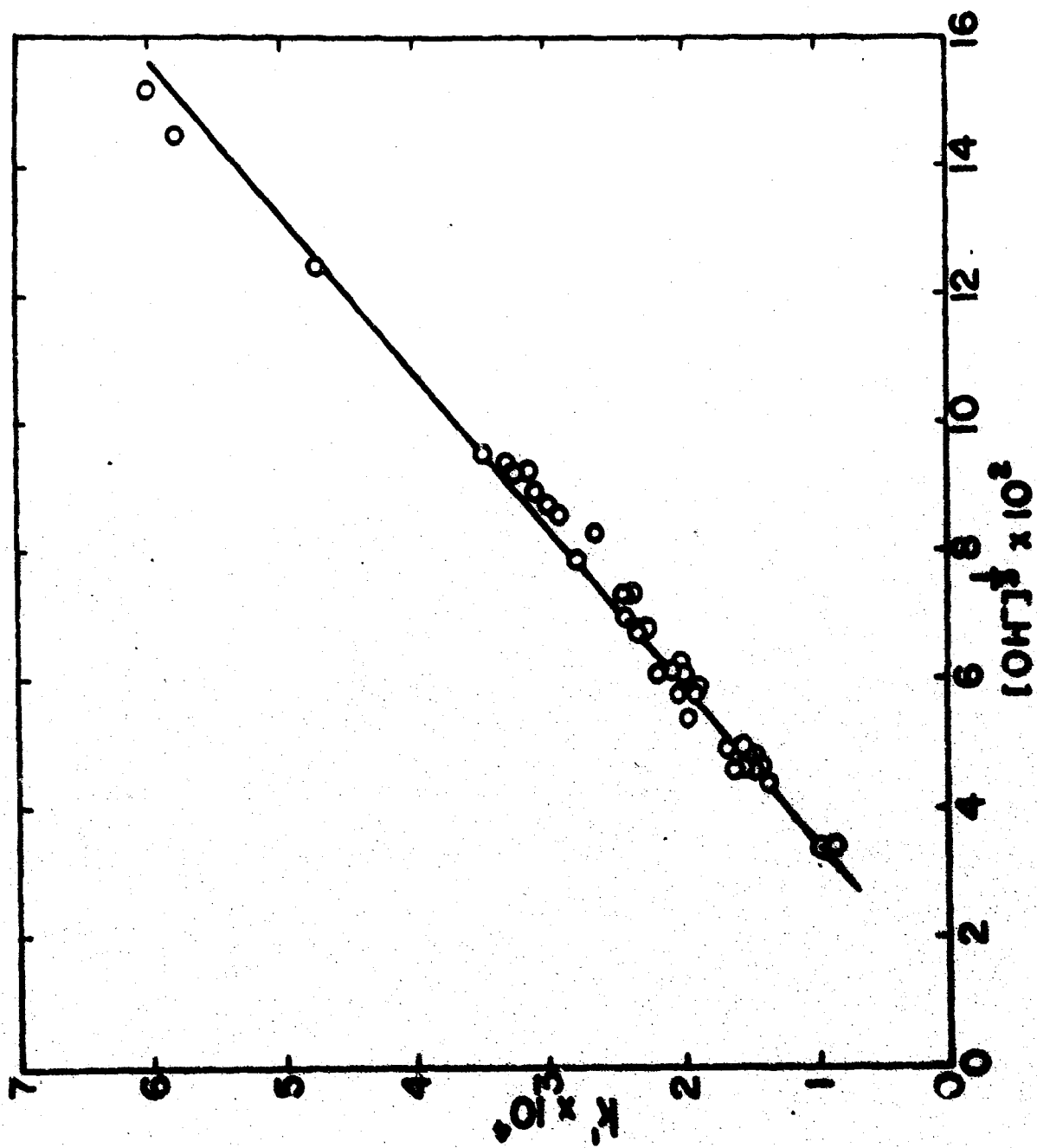
Fig. 3 - Relationship between k' and $[OH^-]^{\frac{1}{3}}$ at 20.0°.
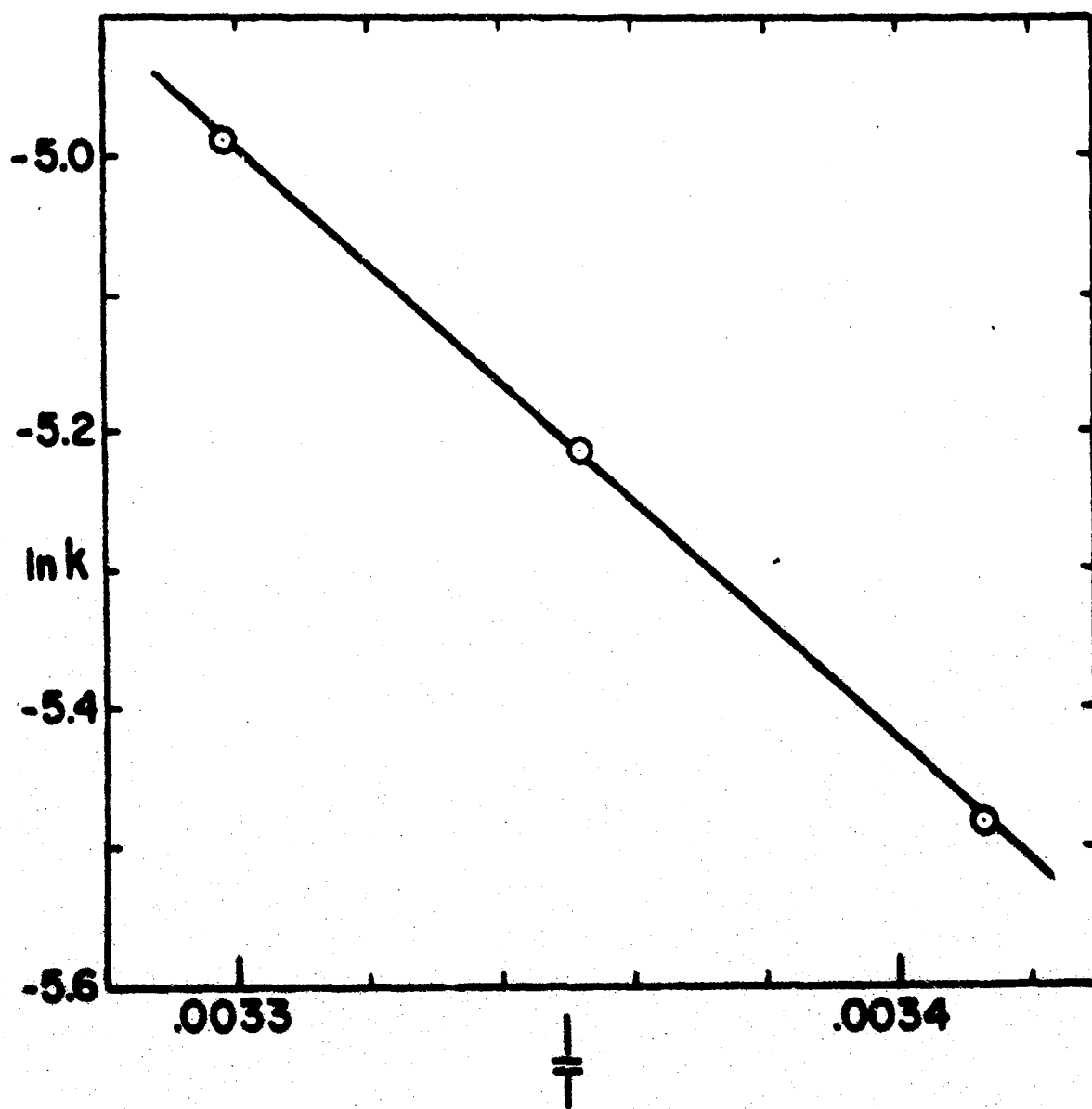
Fig. 4 - Relationship betweek lnk and 1/T when k is the rate constant in the equation $\dfrac{d[OF_2]}{dt} = -k[OF_2]\ ([OH^-]^{\frac{1}{2}} = 0.0105)$

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Oxygen difluoride dissolves in water and reacts only very slowly with the solvent. In alkaline medium, however, the rate of hydrolysis is increased and follows the equation

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